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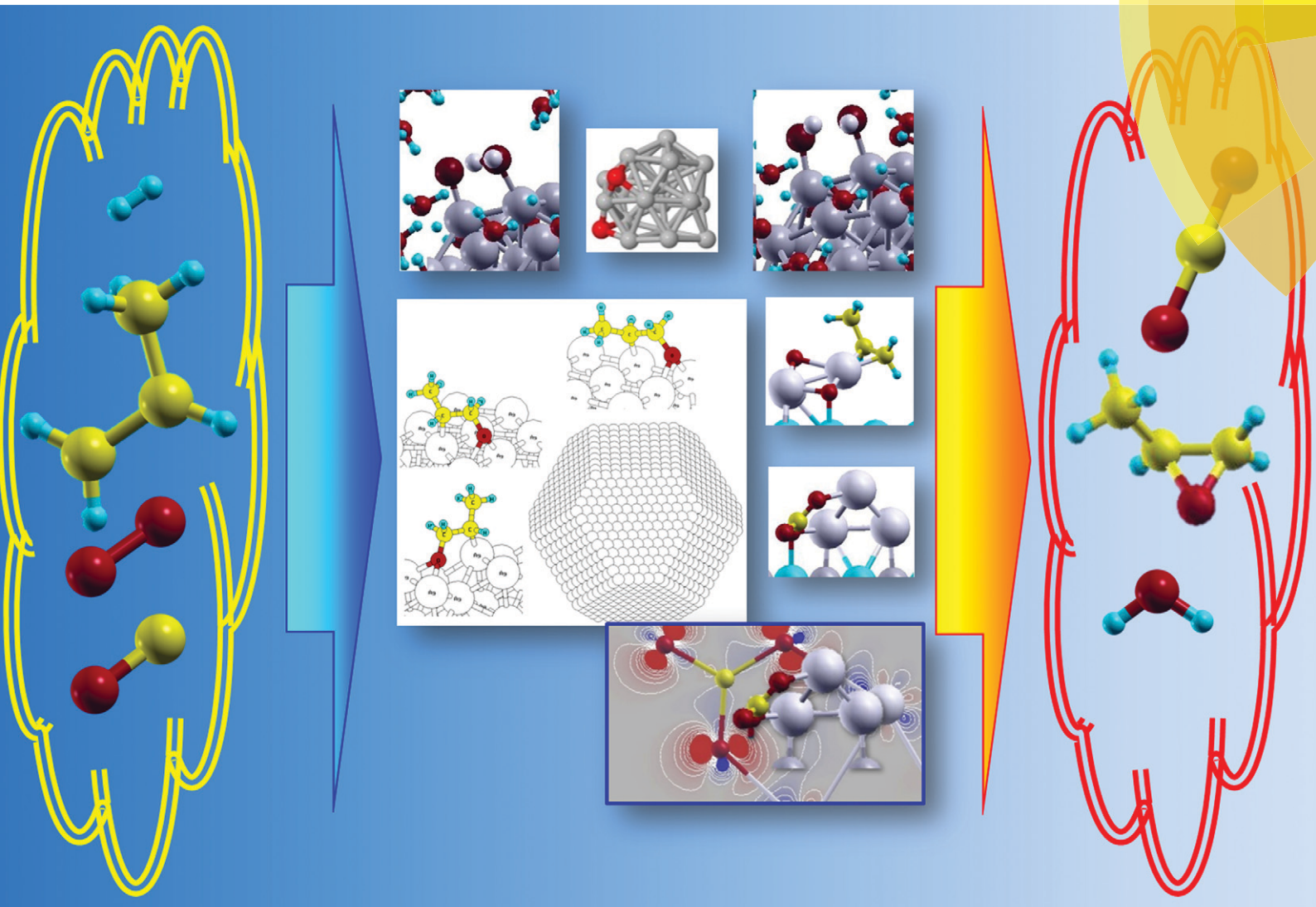

Themed issue: Nanocatalysis

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EDITORIAL
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Editorial: Nanocatalysis

175 YEARS

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EDITORIAL

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Editorial: Nanocatalysis

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Catalysis by metal and metal oxide nano-sized (and smaller, sub-nanometer) structures such as clusters and nanoparticles represents a consolidated field in chemistry. Shaping metals into the (sub)nano regime allows one to modulate both quantitatively (surface-to-volume ratio) and qualitatively (types of facets and surface atom coordination) the catalytically active regions with respect to extended systems. This increased freedom has been widely exploited in the past to improve/maximize the efficiency and selectivity of many catalytic processes of fundamental interest and industrial relevance. Major challenges however exist in the field, which are not yet fully addressed. The transition from carbon-based to green energy production, storage, and use and the environmental implications in fact requires the development of efficient and selective catalytic processes at lower temperature and less extreme conditions than those currently known *e.g.* in the conversion of petroleum and biomass, electrochemical and/or photochemical water splitting and fuel cells, CO_2 reduction to fuels, NH_3 synthesis *etc.*

To face these challenges, recent developments and advances have been realized in three major areas: (i) catalyst preparation and treatment (*e.g.* size selection and control, high precision synthesis of poly-metallic particles, novel nanostructured systems); (ii) nanostructure characterization (especially *in situ*/*operando* characterization of structural, morphological, compositional, and textural properties of catalysts under reaction conditions); and (iii) predictive computational modeling of realistic catalytic systems (*in silico* screening under operating conditions). To these advances, a fourth should be added, that is, (iv) the synergic and cross-disciplinary combination of the previous three areas to achieve interactions and stronger links among different experimental and theoretical techniques for characterizing, synthesizing, and sampling the chemical behavior of such materials. Indeed, a close coupling of experimental synthetic and characterization methods with theory can form a highly complementary multidisciplinary approach towards the design of new catalytic multifunctional materials. To give a few examples: (i) novel nanostructured systems are continuously being synthesized, such as novel particle/substrate combinations, small sub-nanometer clusters that consist of only a handful of atoms with atomic precision, size- and shape-defined few-nanometer particles, nanoalloy synthesis with controlled composition and ordering, and extensive use of novel preparation and impregnation techniques such as atomic layer deposition or deposition of colloidal systems on supports; (ii) impressive progress has been made with *in situ* characterization through synchrotron-based X-ray techniques such as absorption fine structure spectroscopy (XAFS), emission (XES) and photoelectron (XPS) spectroscopy, advanced microscopy such as scanning and transmission electron microscopy (SEM and TEM), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS); and (iii) multi-scale modeling approaches have been and are being developed that, starting from a systematic sampling of reaction paths at the atomistic level, taking explicitly into account realistic reaction conditions of temperature and chemical potentials of reactants, reach the description of processes occurring on macroscopic length scales such as mass and heat transport. The basic idea underlying these developments is that a fundamental understanding of structure/property relationships and of reaction mechanisms at work under realistic conditions can be extremely useful if not *tout court* indispensable for making progress also in technological applications, to realize an informed rational design which can eventually solve the above-mentioned societal challenges.

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These advances have indeed opened novel perspectives in the field for all types of heterogeneous catalysts synthesized under wet chemistry, physical deposition, vacuum or ambient conditions, and have enabled a much deeper understanding of fundamental phenomena such as the evolution of catalytic properties with size and composition, from the smallest atomic clusters consisting only of under-coordinated surface atoms, to middle-sized and larger particles with a changing ratio of facets to corners, edges and core atoms and the associated non-monotonic evolution of propensities to binding, reactivity and catalytic properties, and the associated complex, evolving under reaction conditions, and catalyst structures. Growing evidence is in fact accumulating showing that the status of the catalysts under reaction conditions plays a crucial role in the catalytic activity, hence the need to obtain precise information on how the as-prepared materials evolve once exposed to the reaction environment in terms of the *in situ* oxidation state, coverage, and structural dynamics.

The present themed issue of *Catalysis Science & Technology* offers a representative (although by necessity incomplete) selection of contributions which

Table 1 List of papers that appear in the printed version of this special issue, grouped by theme

Theme	Paper	Topic of the paper	DOI	Approach
(1) Catalysts synthesized by physical methods				
Size-dependent structure	S. Peredkov *et al.*	Investigation of the structure of metallic and oxidized Cu_{35} and Cu_{55} clusters, X-ray absorption spectroscopy	10.1039/c6cy00436a	Experiment
Structure and dynamics	Z. Duan *et al.*	Structure and dynamics of Au_{147} nanoclusters, X-ray absorption spectroscopy, density functional theory	10.1039/c6cy00559d	Experiment & theory
Heterogeneous catalysis	H. Yasumatsu *et al.*	CO oxidation on Si-supported Pt_{30} clusters	10.1039/c6cy00623j	Experiment
Heterogeneous catalysis	J. Nordheim Riedel *et al.*	H_2/D_2 exchange on SiO_2-supported Pt_8 clusters, effect of O_2	10.1039/c6cy00756b	Experiment & theory
Electrocatalysis	R. Passalacqua *et al.*	Interaction of Cu_5 and Cu_{20} clusters with CO_2, voltammetry	10.1039/c6cy00942e	Experiment
(2) Materials synthesized *via* chemical routes				
Catalyst design & synthesis	Z. Lu *et al.*	Using atomic layer deposition for the design of Pd-based nanocatalysts	10.1039/c6cy00682e	Experiment
Properties of thin oxide films	B.-H. Mao *et al.*	Electronic structure of thin oxide films prepared by atomic layer deposition, interactions with oxygen	10.1039/c6cy00575f	Experiment
Heterogeneous catalysis	S.-B. Ivan *et al.*	Nickel oxide in the oxidative dehydrogenation of ethane, effect of phosphorus on catalyst performance	10.1039/c6cy00946h	Experiment
Heterogeneous catalysis	V. Fung *et al.*	Oxidative dehydrogenation of ethane on Co_3O_4 nanorods	10.1039/c6cy00749j	Experiment & theory
Heterogeneous catalysis	M. Zacharska *et al.*	Hydrogen production from formic acid on oxide-supported Au nanoclusters	10.1039/c6cy00552g	Experiment
Heterogeneous catalysis	X. Yang *et al.*	Crotonaldehyde hydrogenation on Pt-titania and Pt-ceria nanoparticles	10.1039/c6cy00858e	Experiment
Heterogeneous catalysis	M. Keppeler *et al.*	Reactivity of CO, NO, O_2 and C_2H_6 on zeolite-supported $Pt_{13\pm2}$ clusters	10.1039/c6cy00182c	Experiment
Heterogeneous catalysis	S. Posada-Pérez *et al.*	CO_2 conversion to methanol on β-Mo_2C and Cu/β-Mo_2C	10.1039/c5cy02143j	Experiment & theory
Heterogeneous catalysis	S. Derrouiche *et al.*	Selective butadiene hydrogenation on AuZn nanoalloy formed from Au/ZnO	10.1039/c5cy01664a	Experiment
Heterogeneous catalysis	Z. Wu *et al.*	Pd–In inter-metallic alloy nanoparticles: highly selective ethane dehydrogenation catalysts	10.1039/c6cy00491a	Experiment
Heterogeneous catalysis	X. Wang *et al.*	Selective gas phase hydrogenation of nitroarenes over Mo_2C-supported Au–Pd	10.1039/c6cy00514d	Experiment
Electrocatalysis	H. A. Miller *et al.*	Hydrogen production by alcohol electroreforming on Au–Pd core shell nanoparticles	10.1039/c6cy00720a	Experiment
Photocatalysis	J. C. Matsubu *et. al.*	Oxygen evolution from water: the effect of the interface on the reactivity of semiconductor-cocatalyst junctions	10.1039/c6cy00548a	Experiment
(3) Computational and theoretical studies				
Catalyst stability	A. Figueroba *et al.*	Stability of ceria-supported single atom Pt, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Cu, Ag, and Au catalysts	10.1039/c6cy00294c	Theory
Heterogeneous catalysis	J. Nevalaita *et al.*	Oxygen dissociation on Mo-doped CaO(001) surface and in the presence of Au atoms and clusters	10.1039/c5cy01839k	Theory
Heterogeneous catalysis	I. Demiroglu *et al.*	Absorption of H_2, O_2 and CO on Au–Rh nanoalloys, size and composition effect, density functional theory	10.1039/c6cy01107a	Theory
Heterogeneous catalysis	J.-X. Liang	CO oxidation on single-atom Ni catalyst supported on iron oxide	10.1039/c6cy00672h	Theory
Electrochemistry	L. Sementa *et al.*	Oxygen reduction reaction on Pt_{38} clusters, molecular dynamics simulations	10.1039/c6cy00750c	Theory

take advantage of these recent developments, and in several cases combine them in a multi-disciplinary effort or discuss them in a broader context and perspective. We thus believe that this issue provides a picture of the state-of-the-art in the field of nanocatalysis, with a balanced mix of applied, fundamental, experimental and computational research, and we hope that it will be of significant interest to both academic and industrial researchers and will trigger further progress in the field, as per our goal in proposing it. For convenience of the reader, Table 1 lists the articles that appear in the printed version of this themed issue, grouped by topic.

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